Studies of Zinc and Lead Chalcogenide Thin Films Grown by SILAR (Successive Ionic Layer Adsorption and Reaction) Technique

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Helsinki 2001

ISBN 952-91-3895-4 (Print)
ISBN 952-10-0155-0 (PDF)

Abstract

Thin films of zinc sulfide, lead sulfide and lead selenide were grown by Successive Ionic Layer Adsorption and Reaction, SILAR-method. The experiments were carried out at room temperature and at normal pressure utilizing aqueous conditions.

This study concentrated on the topographical evolution of the films as a function of thickness of the films. For this purpose scanning electron microscopy, SEM, as well as various operating modes of atomic force microscopy, AFM, were utilized. In addition, the crystallinity and the composition of the films were studied by X-ray diffraction and Rutherford back scattering.

SILAR is based in on sequential reactions at the substrate surface. Each reaction is followed by rinsing which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. Accordingly, a thin film can be grown layer-by-layer and the thickness of the film is determined by counting the deposition reactions. Yet, the growth of zinc sulfide, lead sulfide and lead selenide is not simply two dimensional. Enhanced three-dimensional mode is revealed at certain stages of growth by the topographical studies. In case of zinc sulfide thin films, the development of surface roughness showed a maximum together with the nominal growth rate as a function of the film thickness. Lead sulfide on the other hand had constantly growing roughness. With both materials no increase in roughness was observed after a certain thickness. As deduced from SEM images, the roughest films were lead selenide thin films. The highest growth rates were observed with the roughest films.

In addition to the *ex situ* experiments the early stages of the film formation was studied by *in situ* AFM. According *in situ* measurements the early stages of film growth are sensitive and can be effected by the substrate material.

All the films were polycrystalline and had cubic structure. In THE case of lead sulfide thin films the crystallite orientation was Affected by complexing the lead precursor. Triethanolamine complexed lead acetate solution resulted in a strong (100) orientation starting from very early stages of the film growth. The increase of crystallite size was saturated as also the roughness of the lead sulfide film saturated. During the growth of lead selenide the same lead precursor did not show any preferred orientation.

All the films grown in this work, zinc sulfide, lead sulfide and lead selenide were found to contain very little impurities. Light elements, such as oxygen and hydrogen, were detected in small amounts. Contamination from outside is also possible since samples were not stored in inert conditions. Zinc sulfide thin films had excess of zinc, but lead sulfide and selenide thin films were stoichiometric.

Acknowledgement

I wish to express my profound gratitude to my supervisor Professor Markku Leskelä. His ideas as well as his vast knowledge in the field of material chemistry and, above all, his supporting patience have been crucial for this work to come true.

I owe my warmest thanks to my co-worker Dr. Seppo Lindroos. We had numerous enlightening and stimulating discussions during this study.

I am also thankful to my co-authors Prof. Lauri Niinistö, Dr. Thomas Prohaska, Prof. Gernot Friedbacher, Prof Manfred Grasserbauer, Dr. Roland Resch, Dr. J.A.C. Broekaert and Mr. Jarkko Ihanus. The experience of this fruitful international co-operation taught me a lot.

I would also like to express my gratitude to the personnel of the Inorganic chemistry department with whom I had many learning and helpful discussions.

Finally, my deepest gratitude to my love ones, to my wife Airi and our children Anna-Maria and Antti for being able to constantly sustain and encourage me. In addition, I owe sincere appreciation to my parents for supporting me through all these years.

Financial support from Academy of Finland and Technology Development Centre (TEKES) are gratefully acknowledged.

Berikon, September 2001
Tapio Kanniainen

Abbreviations

AES	Auger electron spectroscopy
AFM	atomic force microscopy
ALCVD	atomic layer chemical vapor deposition
ALD	atomic layer deposition
ALE	atomic layer epitaxy
CBD	chemical bath deposition
CD	chemical deposition, CBD
CSD	chemical solution deposition, CBD
CVD	chemical vapor deposition
ED	electrodeposition
EN	ethylendiamine
ERDA	elastic recoil detection analysis
FM	force modulation microscopy
IR	infrared light
ITO	indium-tin oxide
LFM	lateral force microscopy
LPE	liquid phase epitaxy
MBE	molecular beam epitaxy
NRA	nuclear reaction analysis
PDI-AFM	phase detection imagining atomic force microscopy
RBS	Rutherford backscattering spectroscopy
SEM	scanning electron microscopy
SILAR	successive ionic layer adsorption and reaction-method
TAA	thioacetamide (CH_3CSNH_2)
TEA	triethanolamine ($N(CH_2CH_2OH)_3$)
TM–AFM	tapping mode atomic force microscopy
TU	thiourea ($SC(NH_2)_2$)
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

CONTENTS

1. Introduction

Thin films form the basic for today's electronic components. Even complicated device structures are constructed from thin films, deposited one by one. Thin films can be fabricated in various ways. The techniques can be divided to physical and chemical methods.[1] In physical methods the film material is moved from a target source with some form of energy to the substrate. This technique is widely used in one-component films, like metal films. Chemical film fabrication methods involve chemical reactions and the precursors are mostly components undergoing reaction at the substrate surface or in the vicinity of the substrate. Chemical method for making thin films can further be divided into gas phase and solution methods.

One of the newest solution methods for deposition of thin films is Successive Ionic Layer Adsorption and Reaction, SILAR-method. SILAR is aqueous solution technique based on sequential reactions at the substrate – solution interface for the deposition of thin films. The SILAR was developed by Nicolau for the deposition of zinc and cadmium chalcogenides thin films some 15 years ago.[2]

The most used solution technique and also one of the oldest methods for thin film growth is chemical bath deposition, CBD, sometimes called chemical deposition, CD, or chemical solution deposition, CSD. CBD has been widely used for the deposition of chalcogenides for various applications.[3,4] In CBD all the precursor ions are present at the same time in the reaction vessel. Typically CBD has a so-called terminal thickness indicating a point where the growth of thin film is stopped due to depletion of precursors in the solution. The precursor molecules are metastable releasing slowly ions for the deposition reaction. The product has low solubility, but due to limited number of free ions a direct homogeneous precipitation in the solution is prevented.[3] For metal sources complexed ions are usually utilized. Generally sulfur and

selenium sources are decomposable molecules, like thiourea or thioacetamide and selenourea, respectively.[5-7] The mechanism of CBD process and the effect of various deposition parameters are widely studied. As the deposition conditions change during the deposition process, it can result in different layers, *e.g.* compact inner layer and porous outer layer, in the film.[8]

Another solution-based technique is electroplating or electrodeposition, ED. In ED ions are deposited from the solution by external electrical force onto the substrate. The precursor ions can be with or without complexation and the electrical force can be constant or alternated.[9]

SILAR and CBD have their analogues in gas phase methods. CBD resembles chemical vapor deposition, CVD. In both methods all constituents of the film are introduced at the same time onto the substrate. The chemical reaction takes place either on the substrate or in the gas phase close to the substrate (CVD) or in the solution phase close to the substrate (CBD). Apart from the different phase, another difference is that in CVD the substrate in the reaction space is constantly fed with fresh precursors whereas the CBD is commonly batch type of reaction.[10]

SILAR on the other hand resembles atomic layer epitaxy/atomic layer deposition, ALE/ALD and molecular beam epitaxy, MBE, due to sequential introduction of precursors. Particularly, the saturated surface reactions with ligand exchange mechanism makes SILAR solution analogue of gas phase ALD.[11]

Among the different thin film fabrication methods aqueous solution techniques possess certain advantages. These techniques are cost effective and are technically undemanding to the experimentalist. Furthermore relatively mild conditions are used. The deposition is carried out at or close to room temperature and under normal pressure. Thus it is possible to use

temperature sensitive, *e.g.* polymer substrates. Gas phase methods utilize substantially higher temperatures, up to several hundred centigrades. The basis of gas phase methods is the use and the production of gaseous chemicals. In many cases some of the precursors and by products might be toxic, like hydrogen selenide, or otherwise difficult to handle. Keeping a solution isolated from its environment in most cases is easier than keeping the gas system isolated. In addition, precipitation is a quantitatively effective way to concentrate problematic elements and precursor chemicals.

In spite of the complicated and costly vacuum systems, gas phase methods are widely used for the deposition of thin films. In general, gas phase methods have the advantage of being very fast compared to solution methods. Due to high quality of the CVD grown films, such as purity and crystallinity, this technique is broadly used in industrial scale.

This work studies the growth of zinc sulfide, lead sulfide and lead selenide thin films by SILAR-method. Zinc sulfide is used in light emitting devices. Lead sulfide and -selenide have been known for centuries for their applications in the field of IR-detection. Particular focus is put on the topographical and morphological development of the films during the SILAR growth.

This work is based on following original publications and these are referred to in the text by their Roman numerals.

I) S. Lindroos, T. Kanniainen and M. Leskelä: Growth of ZnS thin films by liquid-phase atomic layer epitaxy (LPALE), Appl. Surf. Sci, 75 (1994) 70.

II) T. Kanniainen, S. Lindroos, T. Prohaska, G. Friedbacher, M. Leskelä, M. Grasserbauer and L. Niinistö: Growth of zinc sulfide thin films with

successive ionic layer reaction and reaction method as studied by atomic force microscopy, J. Mater. Chem., 5 (1995) 985.

III) R. Resch, T. Prohaska, G. Friedbacher, M. Grasserbauer, T. Kanniainen, S. Lindroos, M. Leskelä, L. Niinistö and J.A.C. Broekaert: In-situ investigations of ZnS deposition on mica by successive ionic layer reaction and reaction method as studied by atomic force microscopy, Fresenius' J. Anal. Chem. 353, (1995) 772.

IV) R. Resch, G. Friedbacher, M. Grasserbauer, T. Kanniainen, S. Lindroos, M. Leskelä and L. Niinistö: In-situ investigations on the SILAR-growth of ZnS films as studied by tapping mode atomic force microscopy (TM-AFM), Fresenius' J. Anal. Chem. 358, (1997) 80.

V) T. Kanniainen, S. Lindroos and M. Leskelä: Deposition of lead sulfide thin films by successive ionic layer reaction and reaction technique, Adv. Sci. Technol., 5(Advances in Inorganic Films and Coatings) (1995) 291.

VI) T. Kanniainen, S. Lindroos, J. Ihanus and M. Leskelä: Growth of strongly oriented lead sulfide thin films by successive ionic layer reaction and reaction (SILAR) technique, J. Mater. Chem., 6 (1996) 161.

VII) R. Resch, G. Friedbacher, M. Grasserbauer, T. Kanniainen, S. Lindroos, M. Leskelä and L. Niinistö: Lateral force microscopy and force modulation microscopy on SILAR-grown lead sulfide samples, Appl. Surf. Sci., 120, (1997) 51.

VIII) T. Kanniainen, S. Lindroos, R. Resch, M. Leskelä, G. Friedbacher and M. Grasserbauer: Structural and topographical studies of SILAR-grown highly oriented PbS thin films, Mater. Res. Bull., 35, (2000) 1045.

IX) T. Kanniainen, S. Lindroos, J. Ihanus and M. Leskelä: Growth of lead selenide thin films by successive ionic layer reaction and reaction (SILAR) technique, J. Mater. Chem., 6 (1996) 983.

2. Basics of SILAR

Successive Ionic Layer Adsorption and Reaction-, SILAR-method for the deposition of thin films was introduced by Nicolau in 1985.[2,12] Like stated by the name the method is based on successive reactions of solvated ionic components on the solution-solid interface. Cation $[KL_p]^{n+}$ and anion $[AL'_q]^{m-}$ are reacting forming solid compound K_mA_n. Precondition is that solubility constant of the compound formed by the precursors K and A is low enough. On the other hand the by-products must be soluble in given conditions. The overall reaction can be presented as follows:

$$m[KL_p]^{n+} + n[AL'_q]^{m-} \rightleftharpoons K_mA_n\downarrow + mpL + nqL' \qquad (1)$$

The SILAR-growth is divided (at least) in four different steps presented in fig 1.: i) adsorption, ii) rinsing I, iii) reaction and iv) rinsing II.

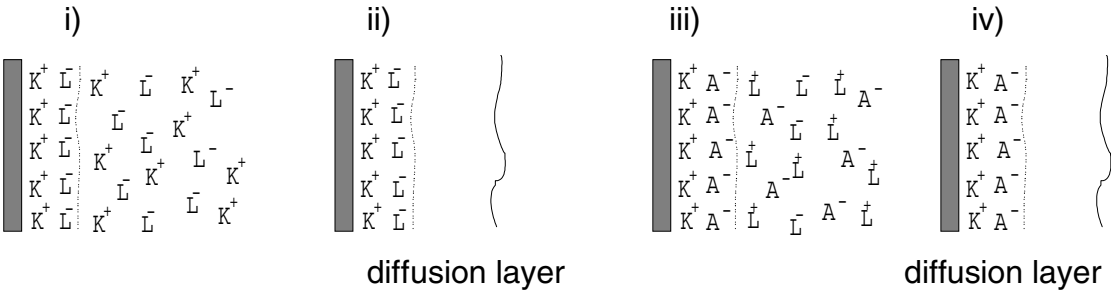

Fig. 1. Schematically presented SILAR growth. i) adsorption of precursor KL_p on the substrate surface and the formation of the electrical double layer, ii) rinsing step I, whereby the excess, unadsorbed ions K^+ and L^- are removed from the diffusion layer, iii) reaction of KL_p surface species with the precursor AL_q' and iv) rinsing II to remove the excess and unreacted species, A^-, L'^+, L^-, and the reaction by-products away from the diffusion layer. The result is a solid layer of the compound K_mA_n. (For clarity the symbols of ions are simplified in the picture compared to eq. 1)

In the first step of a SILAR cycle solvated cationic precursor is adsorbing on the surface forming an electrical double layer. This layer is composed of two layers, from the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative from the counter ions of the cations. Excess, unadsorbed precursor is rinsed away from the diffusion layer. This results in a saturated electrical double layer. In the reaction phase the anion precursor is introduced to the system. Due to the low solubility of the material K_mA_n a solid substance is formed on the interface. The last step rinses the counter ions of both types of precursors as well as the reaction byproducts out of the system. By repeating these cycles a thin layer of a material K_mA_n can be grown.

Following the principle mentioned above the maximum increase in the film thickness per one reaction cycle is theoretically one monolayer. Dividing the measured overall film thickness, nominal film thickness, by number of reaction cycles growth rate can be determined.[13] This gives a numerical value for growth rate under the given conditions. If the measured growth rate exceeds the lattice constant of the material a homogenous precipitation in the solution could have taken place. In practice, however, the thickness increase is typically less than a monolayer.[13]

SILAR resembles in many ways chemical bath deposition, CBD. Both techniques utilize aqueous liquid and relatively uncomplicated apparatuses. The basis of both techniques is the utilization of chemical forces between the ions in the liquid phase and the surface ions. No external energy is needed for the growth of a thin film. In CBD, however, reaction temperature is sometimes elevated in order to increase the growth rate. In CBD all the precursors are present at the same time in the reaction vessel and the reaction rate is controlled by slow release of ions from strong complexes.

On the other hand, the operating principle of the SILAR-method has it's analogue in gas phase methods which is called atomic layer deposition (ALD)

or atomic layer chemical vapor deposition (ALCVD^{TM}) or atomic layer epitaxy (ALE). Both methods utilize the sequential introduction of precursors into the reaction separated by an inert media rinsing/purge. Fundamentally both methods are chemical methods, *i.e.* a film is grown via chemical forces. Accordingly, these methods have the benefit of saturated surface reactions, the growth phenomenas are stepwise, atomic layer by atomic layer. Hence the control of thickness of the growing film is made simply by counting the number of precursor introductions.[11] Further advantages of saturated and sequential surface reactions, like uniformity over large surfaces as well as possibility to achieve highly conformal coatings on uneven surfaces, have been demonstrated for ALD.[14,15]

Due to this similarity of operating principle SILAR has been called liquid phase atomic layer epitaxy (LPALE).[I] Yet, by resembling and reminding the technique called liquid phase epitaxy, LPE, this name is somewhat misleading. In LPE liquidized elements are brought in contact to the substrate one by one. This means the temperature conditions are very different from SILAR. In addition names such as ionic layer deposition, ionic layer epitaxy or layer chemisorption have also been used.[16] In order to avoid any confusion this work uses the name SILAR. The fundamental difference to atomic layer epitaxy technique, ALE, is however the phase, ALE/ALD/ALCVD utilizes the gas phase. In practice also the pressure as well as the temperature are different from SILAR. In gas phase normally a reduced pressure, ~ 10 Torr is utilized at elevated temperature, > 100 °C.

The SILAR-method has been used above all to grow following II-VI semiconducting materials: ZnS,[2,12,13,17-20] CdS [2,19-24], $Zn_{1-x}Cd_xS$ [19,20,25-28], as well as their combinations: $Zn_{1-x}Cd_xS$:In [19] and ZnS:Mn.[19,29] Furthermore, lead and copper chalconides, PbS and CuS, have been grown by SILAR.[16,30] Also the growth of various oxide films has been demonstrated.[31-36] The growth has been carried out on soda lime glass [2,12,13,17-20] and some other substrate materials as single crystalline

(111)Si, (111)Ge, (100)GaAs, {111}InP, (111)CaF_2, (0112)Al_2O_3, (0110)$LiNbO_3$, and polycrystalline Mo, Ti and Ta sheets [2], ITO covered (150 nm) glass, amorphous Corning (7059) glass, quartz as well as the following polymer substrates polyvinyl chloride, polycarbonate and polyester polymer surfaces.[37,38]

Recently, several new materials have been introduced on the list of SILAR-grown materials. SILAR has been utilized for the growth of chalcogenides like AgS, Sb_2S_3, Bi_2Se_3, CoS and CdS.[39-43] However, a closer look at the CdS experiments reported in reference 43 tells that the method used does not fulfill the requirements of the SILAR-principle. By definition SILAR consists of sequential saturated reactions whereby all the excess ions, *i.e.* the ions outside the double layer, are rinsed away before the next reaction. (Fig. 1) Accordingly, the nominal film thickness per one dipping cycle must be equal or lower than the lattice constant of the growing material.[13] Deduced from the growth rate (= film thickness / number of dipping cycles) the CdS-film grew in these experiments 14 nm per cycle, *e.g.* much more than the theoretical maximum (~ 0.3 nm).[43] Although the substrate is dipped sequentially like in SILAR, the rinsing step is obviously not carried out until all the reactant ions are moved away. From the growth mechanism it is likely that the method is a kind of “dipped CBD” rather than SILAR. Similarly, in some of the oxide experiments the growth rate was rather high.[33-36]

The basics of SILAR reactions and method have been thoroughly studied by Nicolau.[2,12,13,19,21] The facts affecting the growth phenomena are the quality of the precursor solutions, their pH values, concentrations, counter ions, the individual rinsing and dipping times as well as the flow rate of the rinsing water and the dynamics of rinsing. In addition complexing agents and the pretreatment of the substrate have been shown to affect the SILAR growth.[2]

3. Experimental procedures

The basic requirement for SILAR thin film deposition equipment is to make it possible for the substrate to contact with the precursor solutions and rinsing media sequentially. Furthermore, side reactions, *e.g.* reactions with oxygen from air have to be eliminated. Essentially the solutions can be in separate vessels and substrate then is moved from a vessel to another. The other option can be that the substrate is stationary and precursor solutions and rinsing media are flown over the substrate. In this work the former principle was used for *ex situ* and the latter was used for the *in situ* studies. In the literature, the majority of the SILAR experiments are carried out with the moving substrate principle.[2,12,13,17-19,21,26,27,33] The flow through principle was found useful in atomic force microscopy (AFM) *in situ* experiments.[44,45] The flow through cell has been also reported for the deposition of PbS thin films with CBD-technique.[46]

The substrates used in this work were soda lime glass, Al_2O_3– and ITO–covered glass and mica. The maximum size of the substrate was 7×5 cm with a thickness of 1 mm. The glass, Al_2O_3– and ITO–covered glass substrates were cleaned ultrasonically, rinsed with acetone and water–ethanol solution and dried in vacuum overnight. Cleaving just before the deposition produced a fresh mica surface.

3.1. *Ex situ* depositions

In the course of this work two types *ex situ* deposition apparatus were used. The first type [I] was similar to that reported in the early SILAR literature.[2,12,13,17-19] Based on the experiences gained with the first apparatus a new apparatus was designed and built. The equipment is based

on a GILSON XYZ robot controlled by a PC. With suitable software this combination makes it possible to control the movements, position and timing, of the substrate accurately. Substrate could be moved in an area of 30 × 50 × 12 cm. The substrate was moved during precursor and rinsing dippings 1 mm sideways with 1 s intervals. The precursor vessels were standard laboratory 250 ml beakers. In the rinsing vessel the rinsing direction was upwards, *i.e.* water was pumped upwards along the substrate with a speed of 200 – 300 ml/min. The substrate, the robot as well as the precursor and rinsing vessels were located inside a controlled atmosphere box where nitrogen was flowd at a rate of ~ 300 ml/min. Before each deposition nitrogen was purged thorough the box for one hour. The apparatus is depicted in fig. 2.

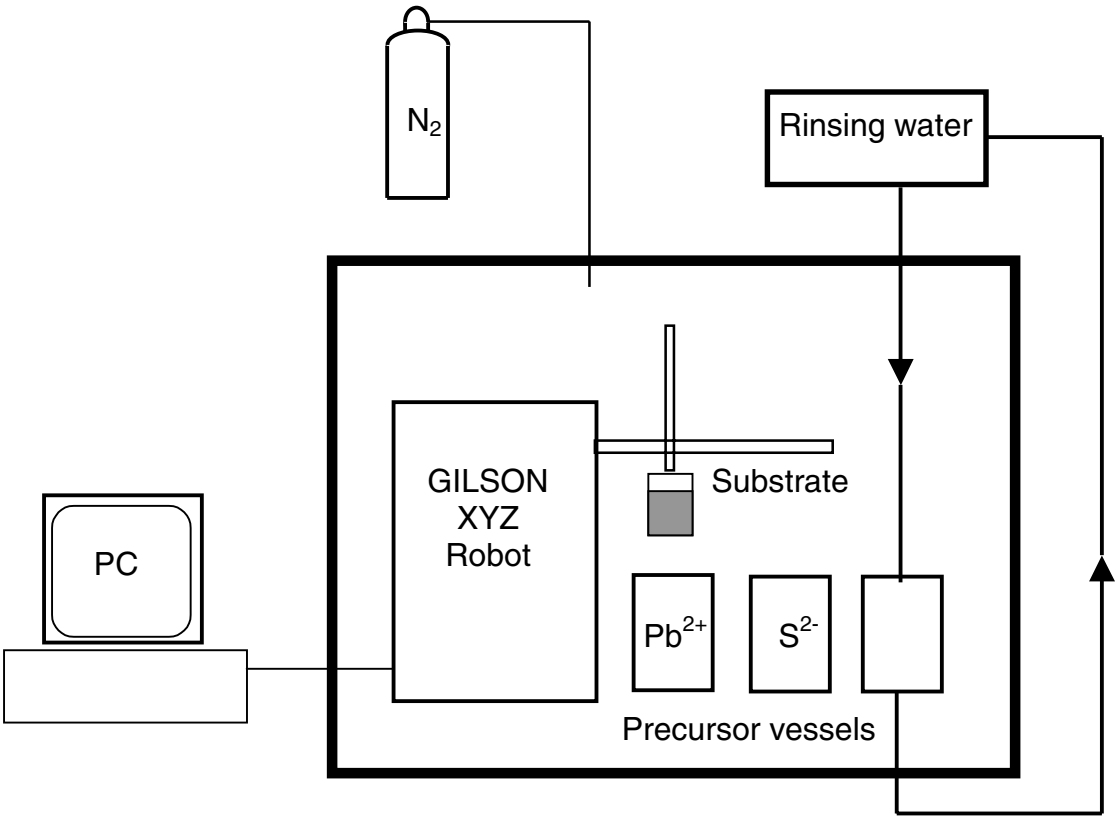

Figure 2. Schematic presentation of the SILAR deposition setup used in this work. The dimensions of the nitrogen filled box were 70 × 70 × 70 cm.

The growth of thin films by SILAR requires very pure water for effective rinsing. Using a flow rate of 240 ml/min consumption in 24 h is about 350 liters. To produce this amount of pure water a water recycling system with closed loop was designed, *i.e.* the water used for rinsing was fed back into a purification unit. The system (Fig. 3) consisted from following units: a Millipore MQ water purification system producing water with 18 MΩcm resistivity with a feeding MQ-pump, two water containers connected together and a continuously running rinsing pump.

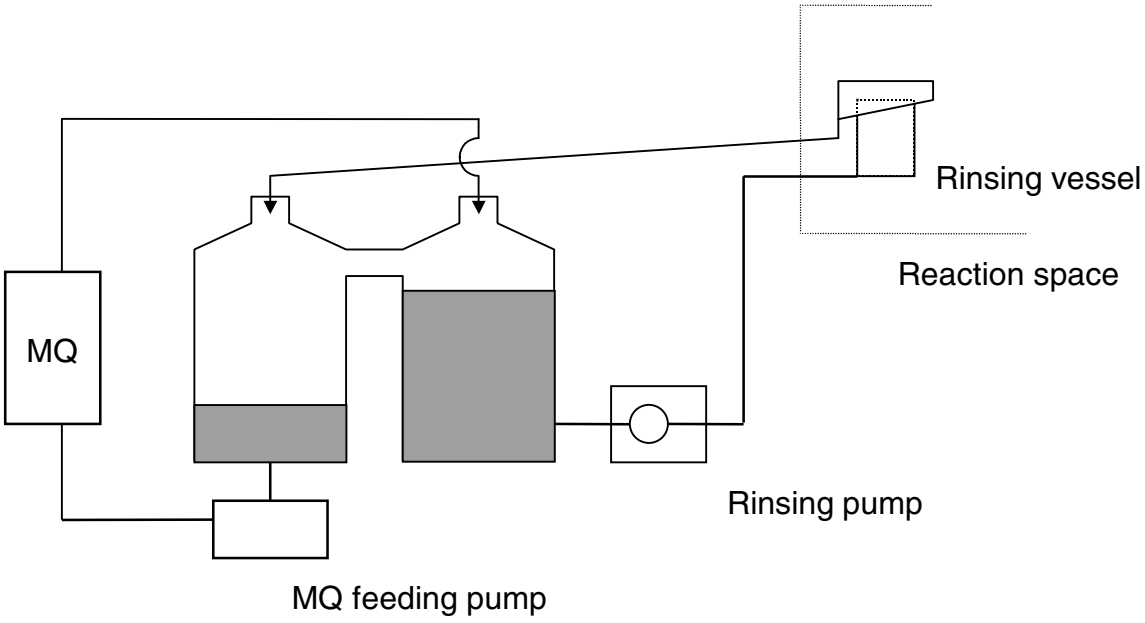

Figure 3. A schematic presentation of the water purification system.

The purpose of the two-container system with connection tube and balanced amount of water was to provide constantly feeding water to the water purification unit itself. The purification system could not be allowed to run dry, otherwise mechanical failure in the pump would follow. The purification effiency of the system was limited by the capacity of ion exchangers. Hence the chemical load, *i.e.* concentrations of the precursor solutions were kept as low as possible.

3.2. *In situ* depositions

Atomic force microscopy (AFM) is a well-suited technique for observation of surfaces both in air and under liquids. The purpose of *in situ* AFM experiments was to study the development of the growth, *i.e*. topography of the growing film during the early stages of the growth.

As opposed to the *ex situ* experiments the substrate was stationary and the precursor solutions as well as the rinsing water flowd over the substrate one by one. The first experiments were done by manually controlling the flows inside the measuring cell with syringes.[II] For subsequent measurements, an automated system (fig. 4), with flow through the cell was used.[III,IV,VII]

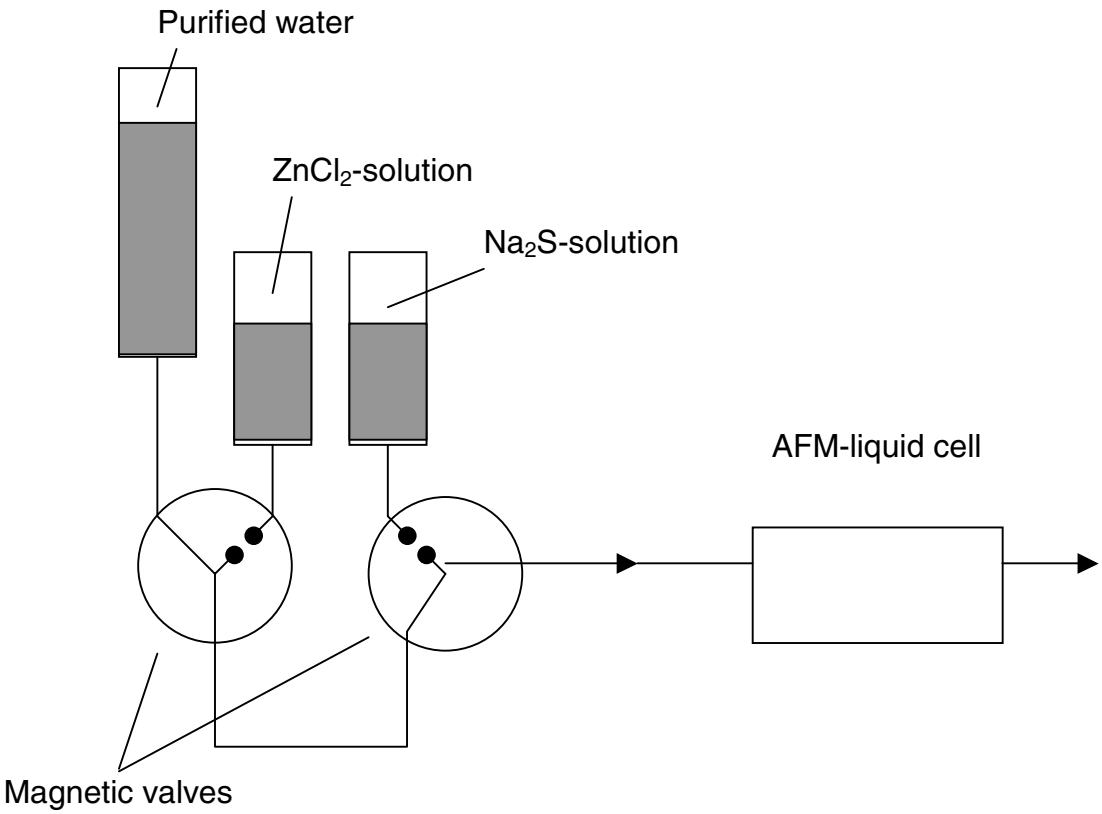

Figure 4. Experimental setup for *in situ* measurement of ZnS thin film SILAR deposition. The controlling PC is omitted from the figure.

The reaction was carried out utilizing disposable solutions. The flow rates and the individual times for each precursor and subsequent rinse had to be determined before carrying out any measurements. The precursor concentrations were the same as in *ex situ* experiments. The substrate was attached with glue to the apparatus. The diameter of the substrate was 1 cm.

3.3. Characterization of the films

Crystal structure and crystallite orientation were determined with Philips MPD 1880 X-ray powder diffractometer system using CuK_{α} radiation. The crystal size was determined by using the Scherrer equation and APD software by Philips.

The thickness of the ZnS films was measured by dissolving the films into hydrochloric acid and measuring the polarographic signal of Zn^{2+} ions with Metrohm 626 Polarograph. The thickness of the ZnS films was also measured by fitting the transmittance spectrum (380 to 820 nm) recorded with HP 8452A spectrometer. The transmittance spectra also provided the refractive indices. The thickness of the PbS and PbSe thin films was obtained by dissolving the films into concentrated nitric acid and measuring the Pb^{2+} ions either by Techron atomic absorption spectrometer, or in a basic media with Metrohm 626 Polarograph. The nominal thicknesess were calculated using the bulk density of the materials.

Chemical composition and thickness of the films were analyzed by Rutherford back scattering (RBS) of 2.0 MV van de Graaff accelerator EGP-10. Hydrogen profiling was carried out by the nuclear reaction analysis (NRA) using a $^{15}N^{2+}$ beam from the 5-MV tandem accelerator EGP-10 to excite the 6.385 MeV of the $^{1}H(^{15}N, \alpha, \gamma)^{12}C$ reaction.

Morphology of the films was characterized with a JEOL JSEM-820 and Zeiss DM 962 scanning electron microscopy apparatuses.

In addition to SEM, atomic force microscopy (AFM) was used to reveal the topography of the growing film. Four types of different AFM measurement modes were utilized: contact force, tapping mode (TM), lateral force (LF) and force modulation (FM). The basic imagining procedure is scanning of a sample surface with a permanent contact, *i.e.* contact force mode. Deflection of the cantilever induced by small forces acting on the tip reveals the samples topography. A further development of contact mode is the tapping mode AFM (TM–AFM). Here, the sample is scanned with a tip mounted on a cantilever that is oscillating at (or near) its resonance frequency with certain amplitude allowing the tip to make transient contact with the sample. Changes in the amplitude reveal the topography of the sample. Since the tip is not permanently in contact with the surface, damages caused by lateral shear forces can be largely excluded. In lateral force mode the torsion or twisting of the cantilever is detected while scanning perpendicular to its length. This torsion increases or decreases depending on frictional characteristics between tip and sample. Force modulation allows the identification of local differences in the sample elasticity by oscillating a cantilever in such a way that the tip indents slightly into the sample.

During *in situ* experiments scanning was stopped and AFM tip was withdrawn from the surface in order to allow undisturbed deposition. However it is to be reminded that the deposition of the thin film was taking place not only on the surface under study, but at every surface in the *in situ* cell. These surfaces include the elastomeric sealing, the cantilever as well as the measuring tip of the cantilever.

4. Growth of zinc sulfide thin films

The precursor solutions for the growth of ZnS thin films were zinc chloride and sodium sulfide solutions. In addition to zinc chloride this solution contained small amounts of sodium hydroxide for adjustment of the pH value.[I]

The growth rate on glass with 0.1 M $ZnCl_2$– and 0.05 M Na_2S–solutions was 0.07 – 0.08 nm/cycle. Using two fold concentrations resulted in two fold growth rate.[I] Similarly to PbS experiments complexing has been shown to increase the growth rate of ZnS. The growth rates were 0.13 nm/cycle and 0.27 nm/cycle with triethanolamine (TEA) and with ethylendiamine (EN), respectively.[47] On (100)GaAs substrate growth rates of 0.16, 0.19 and 0.23 nm/cycle were observed.[22,44,48] Also on polymer surfaces the growth rate was higher, 0.16 nm/cycle, than on glass.[37,38] The growth rate was found to depend on the concentrations of the precursor solutions, by using 5.0 M $ZnCl_2$– and 2.8 M Na_2S solutions a growth rate of 0.30 – 0.31 nm/cycle was achieved.[13] However, the use of high concentrations was not advantageous in practice with the experimental set–up used in this work. Higher concentrations than 0.1 M zinc chloride and 0.05 M sodium sulfide solution caused a very rapid deterioration of the capacity of the water purification system. Hence more concentrated solutions were omitted. Dipping times were tested between 10 – 80 s. Using 10 s dipping times the growth rate was moderate, 20 s was found suitable regarding cycle time and growth rate. The rinsing time was 100 s for the lower concentrations and 200 s higher concentrations.[I]

The growth rate was found to vary as a function of the growth cycles.[I,II] The variation coincidenced with roughness variations.[II] The conclusion was that the ZnS film has different growth modes during the growth, resulting differences in surface area. A rough surface has more surface area, hence a larger growth rate value.[II] With the weaker concentrations as in ref. [I] the

growth rate on polyester surface was 0.22 nm/cycle already at the early stages of the growth, a stabilized value of 0.16 nm/cycle was found after 500 cycles. The high growth rate at the begin was attributed to the rough polymer surface.[38] The thickness measurement is carried out by defining the amount of metal in a dissolved sample of a film. This amount is then related to the area of the substrate, not to the area of the film itself. Hence, the actual area of the film is affecting the measured growth rate. On the other, hand growth rate can also give information about roughness of the film.

Detailed *in situ* studies showed a flattening effect on glass surface during the first ten SILAR cycles because the rms roughness values measured decreased.[II,IV] From 10 to 50 cycles on glass slow and steady increase in the roughness of the growing ZnS thin film was observed, indicating a change in the growth mode from preferentially two–dimensional to preferentially three–dimensional growth mode.[II,IV] *Ex situ* experiments showed a dramatic increase in the roughness of the film between 50 and 200 cycles. Another change in the growth mode took place after 200 cycles, when the ZnS film topography was flattened again. From 400 cycles upwards (30 nm) almost constant rms roughness values of 5 nm were observed.[II]

Comparing the topography of ZnS thin films grown by SILAR on (100)GaAs and on (100)Si to that on glass clear differences are observed. On (100)Si the rms roughness increases steadily reaching 14 nm after 100 cycles.[49] On (100)GaAs the films are the flattest.[44,48] By the nominal thickness of 40 nm the rms roughness had increased rapidly to a value of 1.6 nm and only a slight increase to 1.9 nm was observed with 180 nm thick films.[44] In another study of ZnS on (100)GaAs, 35 nm thick ZnS film had a R_a roughness of 1 nm and a local maximum value of ~ 3 nm as a function of the film thickness was observed at the thickness of 50 nm. At the same time tensile stress of the film reached maximum. A clear minimum in roughness followed at 70 nm. After this thickness, the roughness increased again and stabilized after the thickness of 90 nm to a value of 3.5 nm.

These two studies differ also in defining the point of full surface coverage. On basis of contact force AFM images and the fact that tensile stress started to decrease rapidly at 50 nm finally turning to compressive, it was deduced that the islands coalescenced and full coverage was achieved at this thickness.[48] Whereas based solely on TM–AFM images the surface was found to be fully covered at the thickness of 2.3 nm.[44] For comparison, PDI (Phase detection imaging) AFM revealed contrasts on (100)Si surface whereas TM-AFM was unable to show any topographical changes.[45] Although the interpretation of PDI images is not easy, this demonstrates the limitations of contact force AFM technique in defining the point of full surface coverage.

In comparison to glass surface in films grown on freshly cleaved mica the flattening effect is absent. On the contrary, an increase in roughness is observed from the firsts cycles onwards.[II,III,IV] In one experiment after an increase a slight decrease was observed on mica in rms roughness values.[II] The behavior of mica under water is not straightforward. Although the shape of the curve as a function of the cycles is similar in both cases the values in ref. [III] are ten times the values in refs. [II,IV]. The measurements were made first in water with contact force AFM [II,III] and then in absolute ethanol with tapping mode [IV]. The change was due to possible artifacts caused by the AFM imaging on muscovite in water.[50] Based on the rms roughness values in [III] to the other experiments it is likely that the measurement set up was not the optimum and the result contains artifacts. Furthermore, experiments to grow ZnS on mica *ex situ* failed. The freshly cleaved large mica sheet contained always edges and voids that caused ineffective rinsing resulting in homogeneous growth mechanism and sedimentation of ZnS.

The ZnS films grown on glass were amorphous up to a nominal thickness of 30 nm as studied by XRD. After this thickness the films showed polycrystalline cubic structure with [111] preferential orientation.[I,II] The increase of the cubic ZnS(111) reflection coincidences with the decrease in

rms-roughness.[II] Grown on (100)GaAs substrate a polycrystalline ZnS thin film with weak cubic orientation was observed after a 50 nm thick amorphous phase.[48] In experiments on Ge(111) surface a change in crystal orientation was observed, the growth of ZnS started as hexagonal but changed over to cubic orientation after 12 nm thickness.[20] On (100)Si substrate a weak cubic (200) reflection was detected.[49] In comparison to glass polymer substrates made the SILAR grown ZnS thin films more amorphous. Polycarbonate resulted in amorphous and PVC polycrystalline ZnS thin films.[37] On polyester the films were amorphous up to a thickness of 250 nm, after that crystallization was detected.[38]

The refractive indices of SILAR grown ZnS were between 2.07 – 2.19 on glass substrate and 2.15 – 2.30 on ITO substrate.[I] By complexing the zinc-ions the refractive indices were slightly lower.[38] On (100)GaAs refractive indices increased as a function of the film thickness from 1.75 to 2.10 between 35 and 140 nm measured by ellipsometry.[48] In comparison, ALE method has resulted in higher refractive indices values of 2.30 – 2.41 for ZnS. The higher temperature utilized in ALE enhances phase purity and crystallinity.[51]

According to RBS measurements the ZnS films contained excess of zinc, the S/Zn ratio was 0.8. Also oxygen and hydrogen impurities were found.[I] Similarly, ZnS films grown on (100)GaAs by SILAR were found to be slightly zinc rich containing oxygen.[48] In comparison, IR-studies revealed water in films grown on Ge-substrates, but no hydroxide was found either by IR, or RBS or Auger measurements.[19] On the other hand, EXAFS measurements indicated a presence of hydroxide on the surface layer of the SILAR grown ZnS films.[52]

5. Growth of lead sulfide thin films

Lead sulfide thin films were grown by using lead nitrate ($Pb(NO_3)_2$), lead acetate ($Pb(CH_3COO)_2$) [V] and lead acetate complexed with triethanolamine (TEA, $N(C_2H_5O)_3$).[VI,VII,VIII] The pH values of these solutions were: –nitrate 3.8 –acetate 6.5 and acetate-TEA complex 7.0 – 7.8. Lead acetate-TEA concentration ratio was always 1:2. [VI,VII,VIII] Sulfide precursor was sodium sulfide (Na_2S) [V] and thioacetamide (TAA, CH_3CSNH_2).[V,VI,VII,VIII] Thioacetamide solution had a substantially lower pH value than sodium sulfide solution, 4.7 and ~ 12, respectively.

Growth rate, particle size and orientation were affected by the lead precursor solution. The parameters were the same for each solution, 0.2 M concentration, 20 s dip time, 100 s rinsing time and 250 ml/min rinsing water flow rate. The growth rate was the slowest with lead nitrate solution, 0.02 nm/cycle.[V] Lead acetate solution resulted in a growth rate of 0.06 nm/cycle, whereas the TEA complexation increased the growth rate to 0.12 nm/cycle.[V,VI] Overall, the growth rate was linear as a function of the growth cycles.[VIII] For the PbS grain size the complexation did not have any effect, both of the lead acetate solutions produced a similar grain size. The nitrate solution, on the other hand, resulted in a reduced grain size compared to that of the acetate precursor solution.

The PbS thin films grown by SILAR were polycrystalline cubic with varying degree of orientation. Table 1 displays the relative intensities of XRD reflections of PbS thin films grown with different lead precursor solutions. The pattern of PbS powder is presented in comparison. On glass substrate lead nitrate results in a polycrystalline PbS with a pattern close to that of PbS powder. Lead acetate caused the film to orientate to the [200] direction and the TEA complexed lead acetate solution increased the orientation of the PbS thin film into [200] direction. In fact, no reflections other than this were

detected. Polycrystalline ITO substrate caused [111] orientation to the films grown from lead nitrate and –acetate. With TEA complexed lead precursor the (200) reflection was still the strongest also on the ITO substrate.

Table 1. Relative X–ray diffraction intensities of PbS thin films grown on soda lime glass and on ITO–covered soda lime glass by SILAR with different precursor solutions. Corresponding PbS powder intensities are presented for comparison.[53] (Lead precursors: 0,2 M $Pb(NO_3)_2$, 0,2 M $Pb(CH_3COOH)_2$ and 0,2 M ($Pb(CH_3COOH)_2$) + 0,4 M TEA. Sulfide precursor: 0,4 M CH_3CSNH_2.)

	$Pb(NO_3)_2$		$Pb(CH_3COO)_2$		$Pb(tea)_2^{2+}$		PbS powder
h k l	Glass	ITO	Glass	ITO	Glass	ITO	
1 1 1	53	100	13	100	0	50-80	84
2 0 0	100	96	100	97	100	100	100
2 2 0	23	24	5	33	0	30	57
3 1 1	11	17	3	14	0	20	35
2 2 2	5	8	2	11	0	10	16
4 0 0	4	8	5	11	4	-	10

In absolute values the acetate complexed with TEA resulted in even more pronounced orientation. The XRD intensity of the (200) reflection as well as the crystallite size increased steadily from a few cycles. After a thickness of ~ 30 nm no further increase was observed in these parameters.[VIII]

In comparison to the ZnS thin films grown from complexed zinc–ions there are differences as well as similarities.[47] In both cases the growth rate was enhanced and morphology increased.[47,V,VI] But contrary to the results obtained with lead, the crystallinity and crystallite orientation were suppressed by the use of complexed zinc precursor.[47]

The same precursors, *i.e.* lead acetate–TEA together with TAA, which made the PbS thin film to orientate in SILAR yielded in CBD a polycrystalline

PbS.[54] On the other hand, strongly (200) oriented PbS thin films have been reported on (111)Si substrate as well as epitaxial PbS on (100)Ge and (100)InP using lead nitrate and thiourea, TU, solutions.[55,56] Electrodeposition of PbS on SnO_2 covered glass resulted in polycrystalline cubic thin films with no preferred orientation.[9]

The topography of the PbS films was studied by atomic force microscopy. The rms roughness increased rapidly from the first cycles. Based on the contact force AFM and SEM images the film seemed to construct on separate islands up to a thickness of 30 – 40 nm. [VIII] However, LFM (lateral force microscopy) and FM (force modulation) revealed formations already after 50 cycles (~ 2 nm nominal thickness) indicating full surface coverage.[VII] Hence the growth of PbS follows the Stranski – Krastanov mode.[57] The rms roughness reached a value of ~ 30 nm at the nominal thickness of 60 nm. The smallest grain size was achieved with lead nitrate precursor solution, but the complexation did not affect the grain size when lead acetate solution was used.[V,VI]

According to RBS analysis the PbS thin film grown with the TEA-complexed lead acetate solution was stoichiometric. In addition 6 – 8 at-% light (such as H, C, N or O) impurities were detected.[VI] Galena (PbS) has been shown to react slowly with air forming lead hydroxide, carbonate and hydrogen carbonate and finally lead sulfate as studied by XPS.[58,59] As the SILAR grown PbS samples were not isolated from the air the origin of these, possible atmospheric, impurities cannot be exclusively determined.[VI] Also in PbS thin films manufactured by CBD oxygen was detected. Samples analyzed by AES (Auger electron spectroscopy) contained oxygen on the surface of the PbS as well as on the interface PbS-Si.[5] For comparison, electrodeposited PbS thin films were stoichiometric PbS, but contained less impurities, 1.7 – 2.0 atom% hydrogen and 1.3 – 1.9 atom% oxygen measured by ERDA (elastic recoil detection analysis) and deuteron induced reactions, respectively.[9]

6. Growth of lead selenide thin films

Together with lead sulfide, lead selenide is one of the oldest CBD grown materials. In this work the selenide precursor was freshly prepared from sodium selenosulfide solution similar to CBD process for ZnSe.[7] The lead precursor was the same as used for the growth of PbS thin films, lead acetate complexed with triethanolamine. In comparison to lead sulfide the growth rate for PbSe was higher, 0.18 nm/cycle at the beginning and then after a thickness of 100 nm 0.16 nm/cycle.[IX] Another difference to PbS was the lack of orientation in PbSe thin films. The films were polycrystalline cubic without preferred orientation. Likewise, the PbSe thin films grown by CBD on glass substrate are generally polycrystalline cubic.[60] Also electrodeposition resulted in polycrystalline PbSe thin films.[61]

By visual inspection the PbSe films were mirror-like metallic and smooth. But SEM studies revealed that the morphology was rough, possibly affecting the high growth rate, too.[IX] Analogous rough morphology was found in PbSe thin films deposited by ED.[61] CBD grown PbSe thin films were characterized by relatively high degree of porosity when compared with CBD grown PbS thin films.[62] By studying the MBE growth of PbSe on CaF_2 substrate with AES it was found out that the growth was three–dimensional and several hundred monolayers were needed to form a complete PbSe layer.[63]

The stoichiometry of SILAR grown PbSe was found to be 1:1 within the limits of RBS technique. Impurities detected were 5-atom% of oxygen and 8-atom% of hydrogen.[IX] Similarly ED grown PbSe thin films were also stoichiometric and contained oxygen and hydrogen impurities.[61] The oxygen and hydrogen impurities are commonly related to aqueous conditions in SILAR, CBD and ED depositions. However, also high vacuum gas phase MBE produced PbSe thin film with oxygen impurity, with composition of

$Pb_{0.41}Se_{0.44}C_{0.08}O_{0.06}$ analyzed *in situ* by X-ray photoelectron spectroscopy, XPS.[63] Moreover, carbon and oxygen contamination on the surface of PbSe grown by MBE was detected by XPS and AES if the sample was exposed to air, but a chemical passivation of the PbSe with sulfur resulted in samples without these impurities.[64]

7. Conclusions

During this work the growth of zinc and lead sulfide as well as lead selenide by SILAR was studied. The depositions were carried out at room temperature and at normal pressure utilizing aqueous conditions. Focus was on the topographical development of the films as a function of thickness. SEM, AFM and XRD were used for characterization of the films.

According to the theory of SILAR the thickness of the film is directly proportional to number of deposition cycles. In fact, the development of certain nominal thickness is not a straightforward issue, particularly for the thinnest films. The growth of zinc sulfide, lead sulfide and lead selenide show that in reality three–dimensional mode is dominant at certain stages of growth. Especially at the early stages films are rough, formation of a continuous film cannot be simply derived from the nominal growth rate. Based on various AFM measurements made in different modes the growth is not a pure three–dimensional but a mixture of two– and three–dimensional.

To study the early phases of film formation *in situ* AFM was utilized. It was shown that *in situ* study of SILAR process is possible. However, the sensitivity of surface at the early stages of film formation requires the interpretation of all the data obtained with various operation modes of AFM. Pure contact force does not always coincide with other AFM information. *In situ* studies of ZnS revealed substrate surface dependent behavior. Although the glass surface showed flattening effect at the beginning of the growth, the films had a rapid roughening. However, at the end the films were flat again. The development of surface topography in zinc sulfide was found to coincidence together with the nominal growth rate. PbS thin films, on the contrary, had constantly growing roughness. But like ZnS, after a certain thickness, 60 nm, PbS also showed no increase in roughness. On the basis of SEM images the roughest films were PbSe films. On the basis of these results the roughest films also

had the highest growth rates. Furthermore, complexation increased growth rate of PbS.

All the films were polycrystalline and had cubic structure. The crystallite orientation of PbS films was effected by complexing the lead precursor. TEA complexed lead acetate solution resulted in a strong (100) orientation. Orientation was detected from the very early stages of the PbS film growth. In comparison, ZnS required tens of nanometers thickness before crystallization was detected. The growth of PbS crystallite size was saturated as also the roughness saturated. The use of same lead precursor for the growth of PbSe did not show any preferred orientation.

The PbS and PbSe films grown by SILAR in this work were stoichiometric but ZnS thin films had an excess of zinc. All films contained some impurities. A few atom% of light elements, such as oxygen and hydrogen were detected. Whether these are due to aqueous growth conditions or due to atmospheric origin after the growth of the films cannot be exclusively determined.

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